APPENDIX J. HYDROGEN CYANIDE ANALYSIS

J.1 HYDROGEN CYANIDE REPORT

This work was contracted with the US Army Aberdeen Test Center and performed by Dr. Steven H. Hoke of the Chromatography Analysis Division.

TEST #: 1 Sprinkler September 5, 2003

TEST #: 2 No Sprinkler September 10, 2003

ORGANIZATION: NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY, GAITHERSBURG, MD

TEST FIXTURE: Rhode Island Test

SETUP: Two sampling positions were used to conduct real-time hydrogen cyanide analysis on two different test days at NIST. The two sampling positions were designated position 1 (West – NIST Location D) and position 2 (East- NIST Location C), and were 3.66 m and 1.83 m west of the stage, respectively. Each sample position was located 1.5 m off the floor and 2.74 m from the south wall of the compartment (Figure J-1).

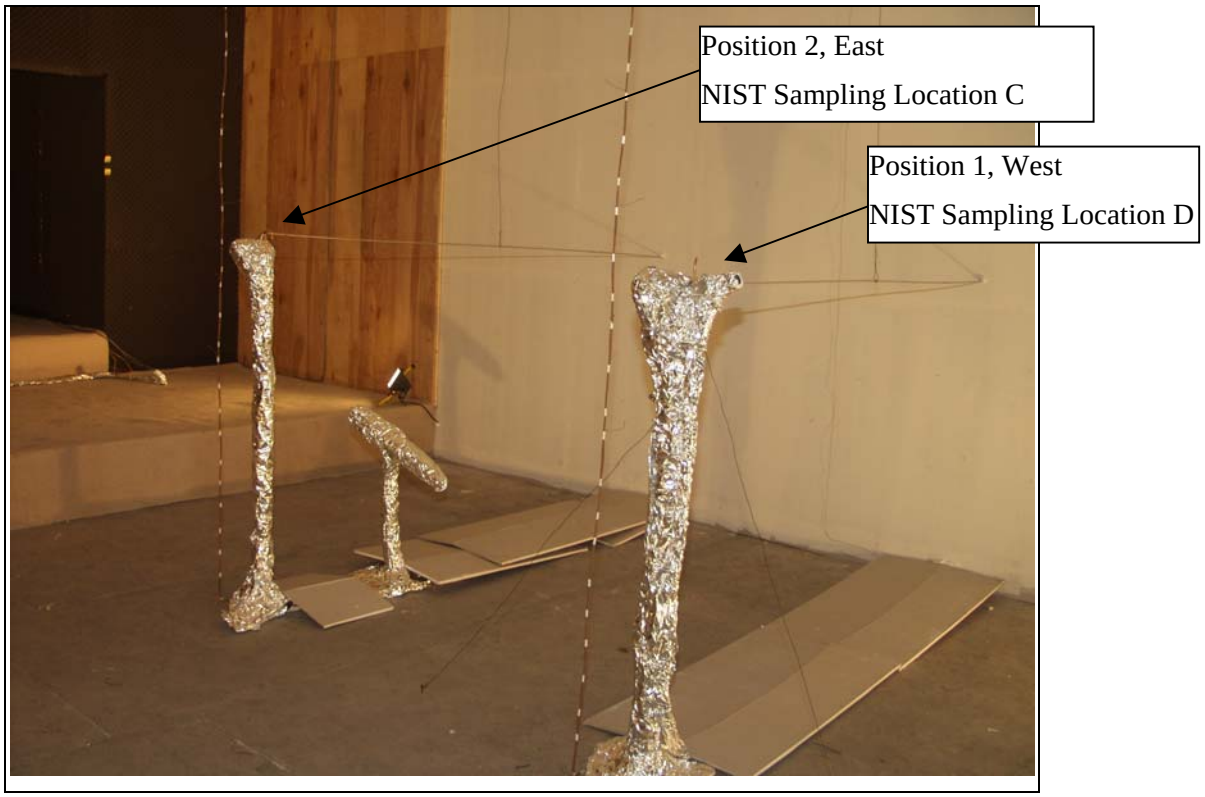


Figure J-1. Sampling positions inside Rhode Island test fixture.

The Sampling equipment was located on a table just outside the south wall of the compartment. Air samples were taken through a ¼-in. o.d. 304 stainless steel tubing. An additional 3 ft. of stainless steel tubing was placed on the outside to provide for cooling of the hot sample gases. A stainless steel 4-port sampling manifold using Swagelok tees was attached to the end of each sample line. Red silicone tubing was used to attach samplers to the manifold (Figure J-2).

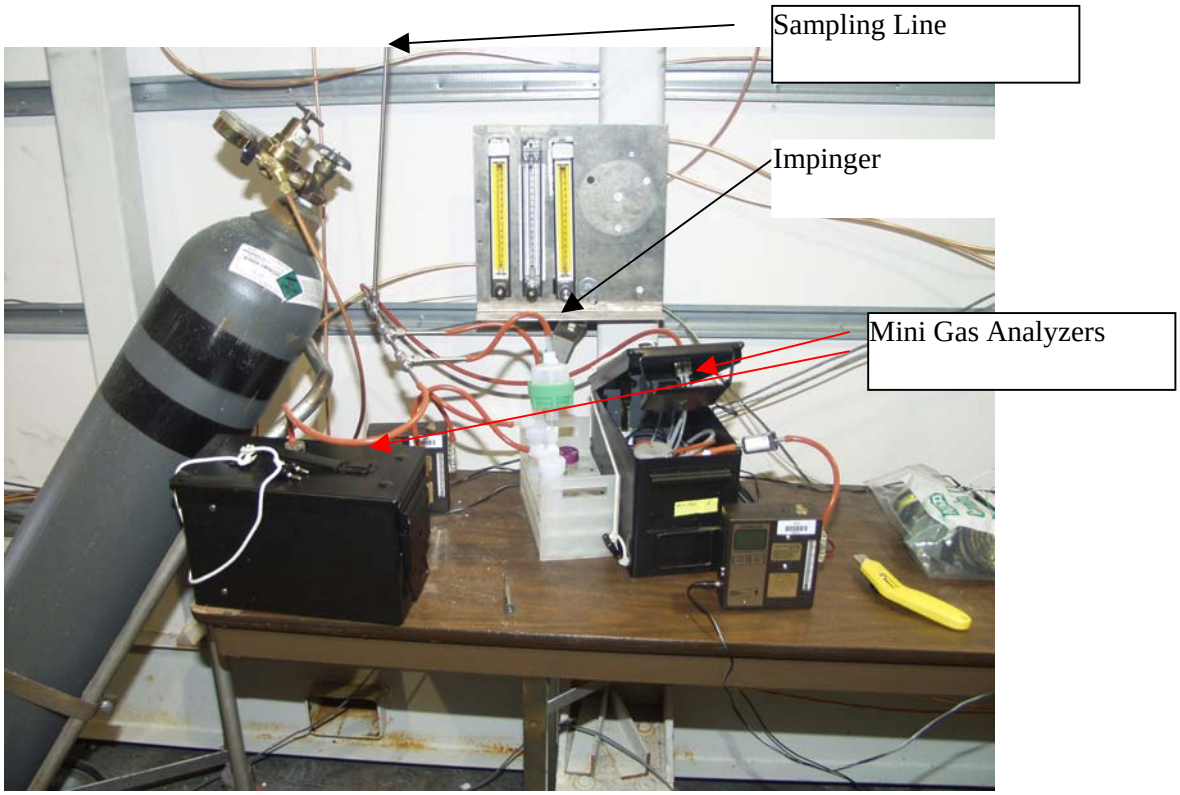


Figure J-2. Sampling set up at Position 1 for test 1.

At each sampling position two impinger samples were taken, one with a filter and one without. Each of these impingers used 0.1 M KOH as trapping solution. For the first test two mini gas real-time cyanide analyzers were used at position 1 and a suitcase-size version of the analyzer was used at position 2. For test 2 a mini gas analyzer was used at each position. Airflow rates were measured and recorded before each test. Voltage signals from the analyzers were recorded on data loggers and also sent to the main control computer.

With the high gas temperatures anticipated a 3-ft. extension of stainless steel tubing was attached between the exterior wall and the sampling manifold. To determine the cooling effect this had on the sample gases, a T type thermocouple was attached to the stainless steel tubing just outside the wall and one just before the sampling manifold. A Fluke model 2635A Hydra Series II Data Bucket collected data from each of the

two thermocouples. This data was only collected for the second test because higher temperatures were anticipated.

After the second test both of the 9-ft. stainless steel lines were removed from the test fixture and rinsed in a vertical position with 10 mL of 0.1 M KOH.

Upon returning to the laboratory the filters were weighed and then placed in a screw cap-polypropylene test tube with 10 mL of 0.1 M KOH.

After each test the contents of the impingers were transferred to a test tube and labeled.

Impinger samples were analyzed according to NIOSH Method 7904.

The real-time mini gas analyzers as described elsewhere (Paper submitted to J. Process Anal. Chem. for publication) were modified to use an off-the-shelf cyanide combination electrode and 0.1 M KOH as the trapping solution. Calibration standards were prepared in 0.1 M KOH using KCN at levels of 2, 5, 10, and 30-ppm cyanide. This corresponds to an upper and lower calibration limit in air of 153 and 10 ppm HCN, respectively. The gas analyzer showed linearity up to 1284 ppm HCN in air, so the high values obtained during the second test can be considered valid.

RESULTS:

Figures J-3 to J-5 show real-time results from the three HCN gas analyzers used for test 1conducted on 5 Sept 03. The automatic sprinkler system activated at about 25 sec.; therefore, there was very little HCN produced.

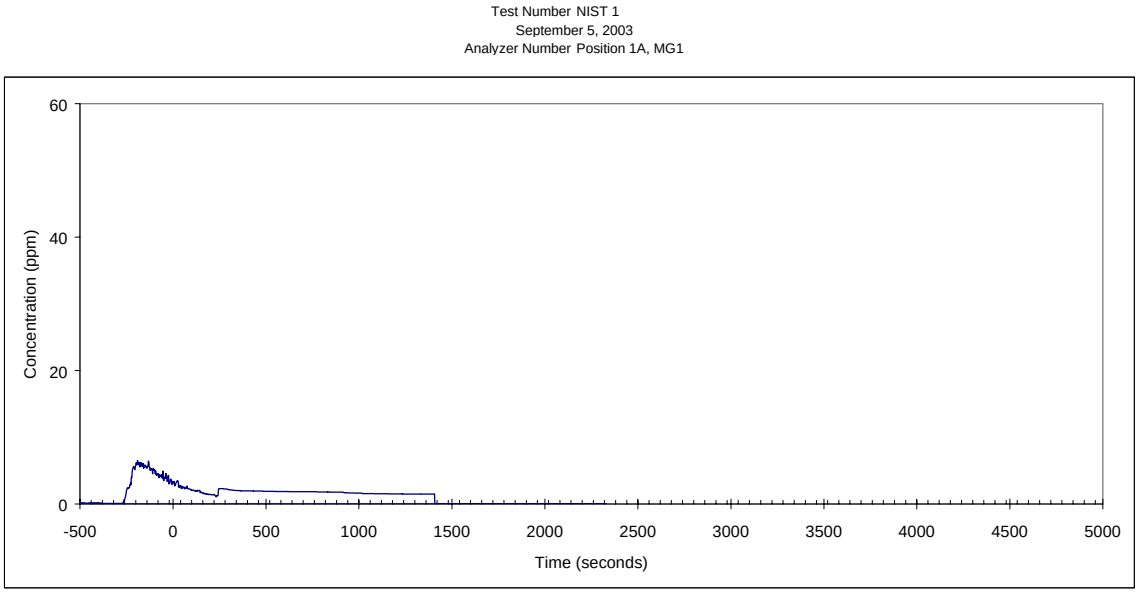


Figure J-3. Hydrogen cyanide response from mini gas analyzer located at position 1.

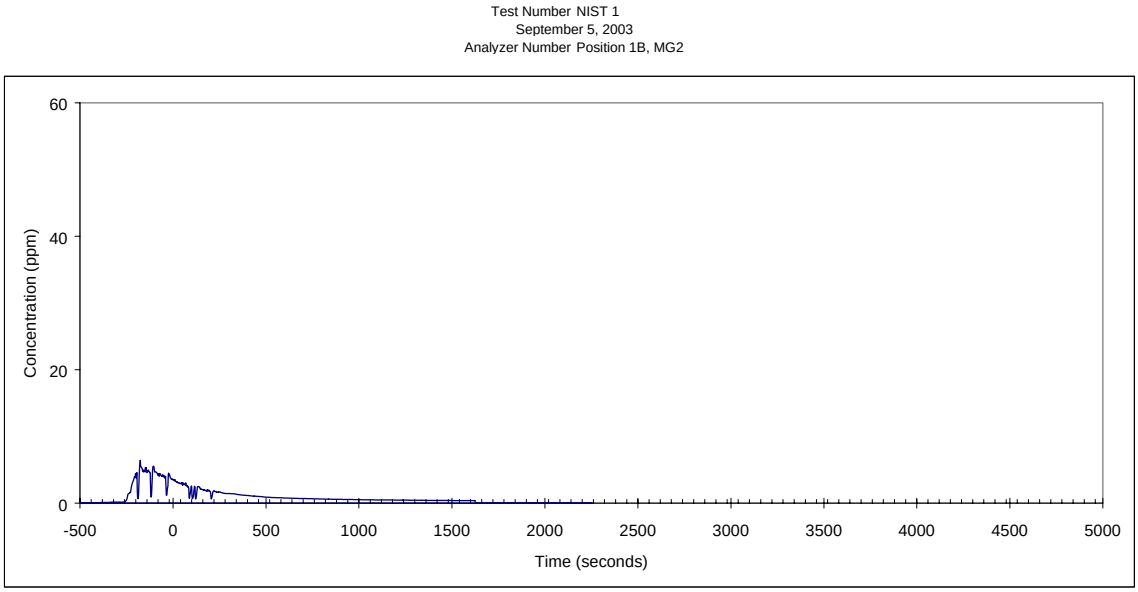


Figure J-4. Hydrogen cyanide response from mini gas analyzer located at position 1.

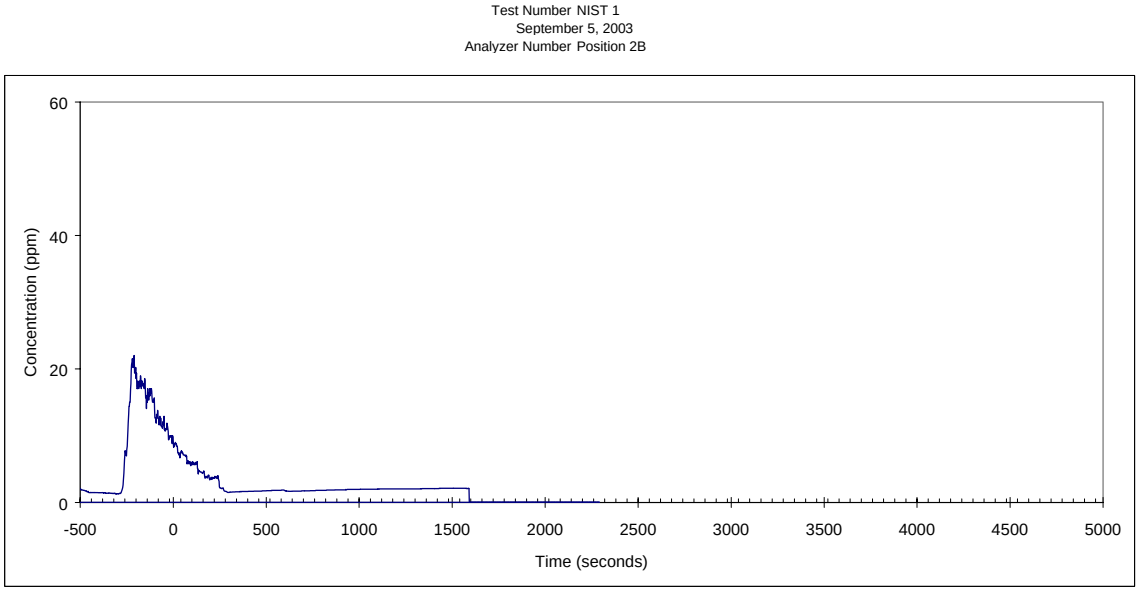


Figure J-5. Hydrogen cyanide response from large gas analyzer located at position 2.

Figures J-6 and J-7 show real-time results from the two mini gas HCN analyzers used for test 2 conducted on 10 Sept 03. This fire burned much longer and as indicated by the response produced much higher values of HCN.

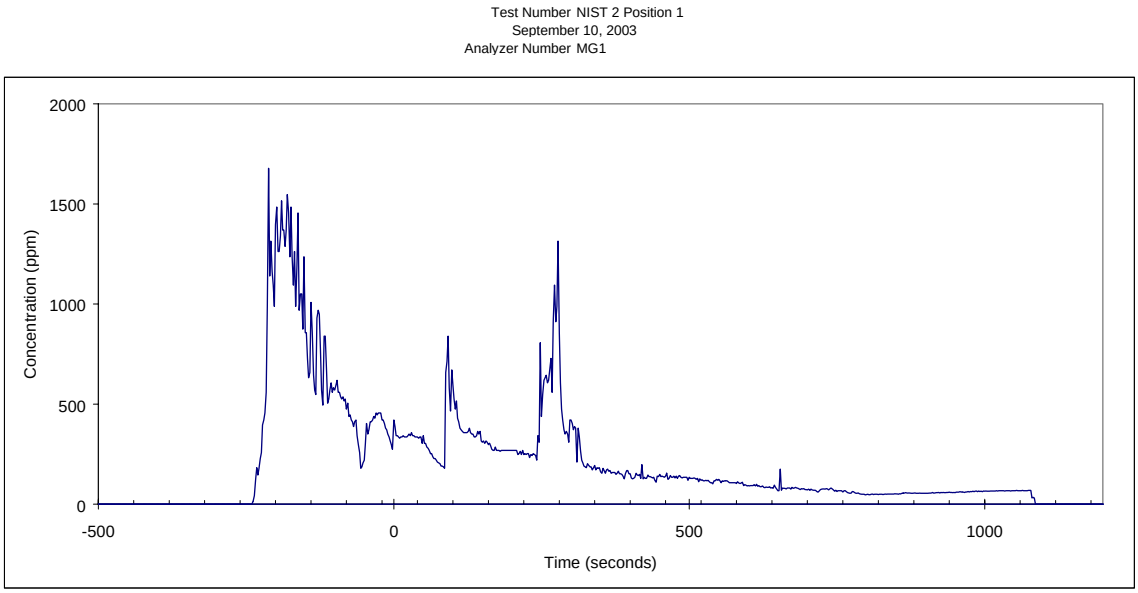


Figure J-6. Hydrogen cyanide response from mini gas 1 located at position 1

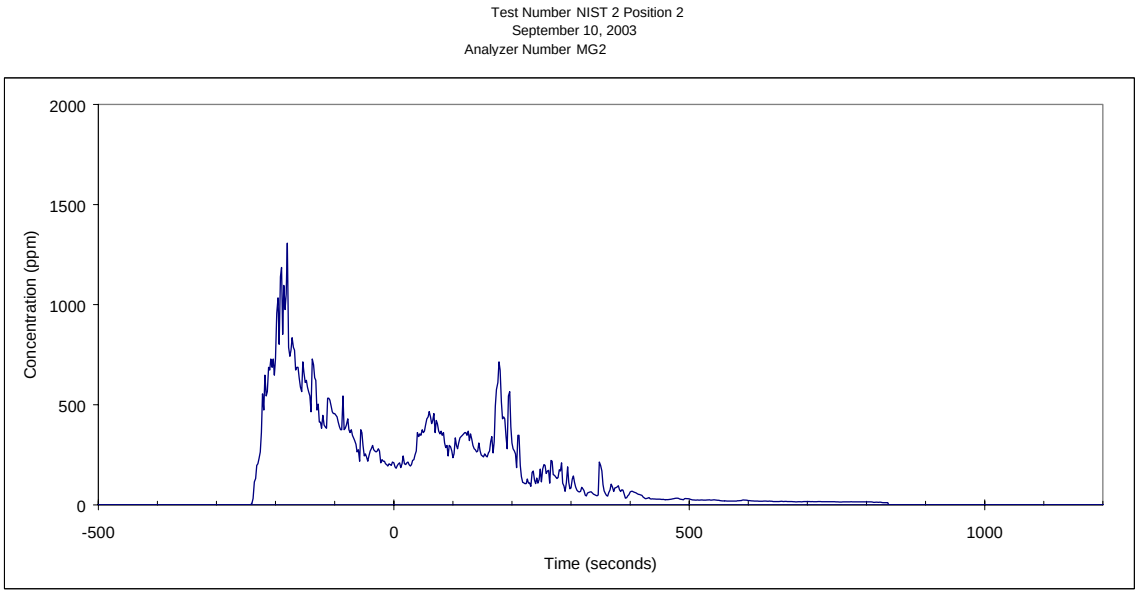


Figure J-7. Hydrogen cyanide response from mini gas 2 located at position 2.

Impinger and filter samples were analyzed according to NIOSH method 7904.

Table J-1. Impinger data for Rhode Island Tests.
(All values reported in ppm HCN for the indicated run time.)

Position	Test Date	Impinger ppm HCN	Impinger (Filter) ppm HCN	Filter ppm HCN	Run Time
1 (West) (NIST Sample Location D)	5 Sept 03	5.0	4.7	BDL	8 min.
2 (East) (NIST Sample Location D)	5 Sept 03	5.1	5.0	BDL	8 min.
1 (West) (NIST Sample Location D)	10 Sept 03	213	153	BDL	1.67 min.
2 (East) (NIST Sample Location D)	10 Sept 03	248	176	BDL	1.67 min.

BDL= Below Detection Limit of 2.5 ppm.

For example at Position 1on 5 Sept 03 the impinger measured an 8-min. TWA of 5 ppm HCN. At Position 1 on 10 Sept 03, a TWA of 213 ppm HCN was measured over a time of 1.67 min.

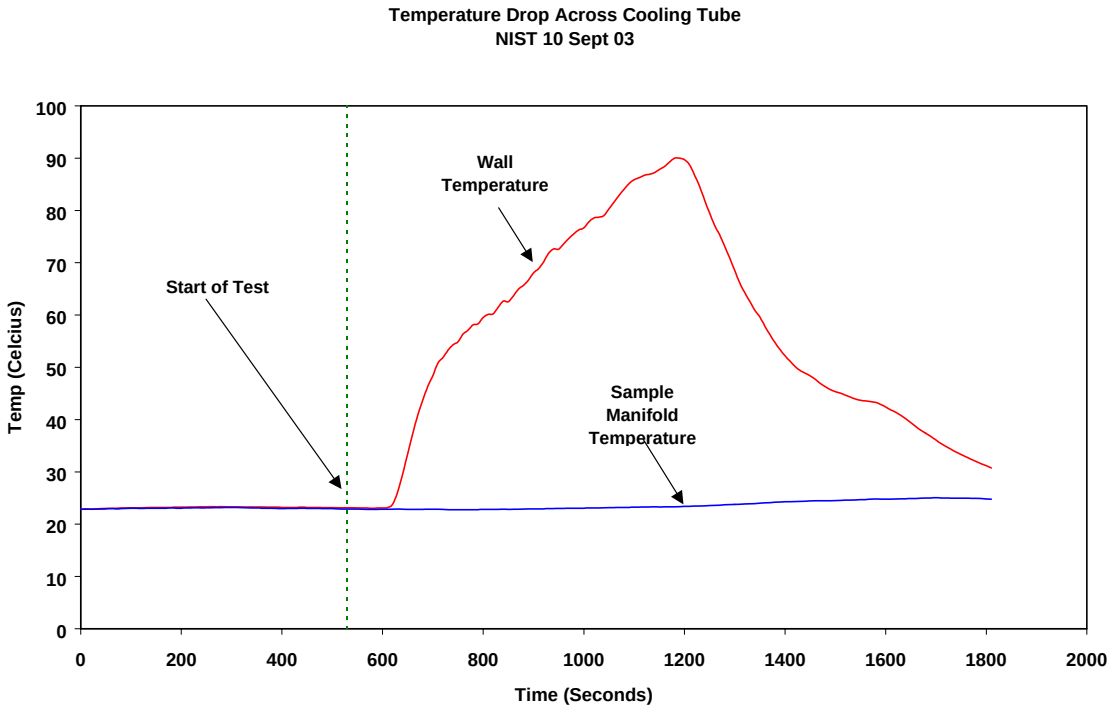
The impinger values may be low compared to the gas analyzer values because the impinger bubbler may not quantitatively collect aerosol forms of HCN.

The impingers behind the filters were expected to be lower than those of the impingers with no filters because any HCN collected on the filters, as aerosols would not be part of the impinger measurement. Because of the large amount of particulate matter on the filter, it was decided to estimate the total weight on the filter prior to cyanide analysis. However, any aerosol forms of HCN on the filters from test 2 were lost because of the time required to obtain filter weights.

The filters were photographed after the second test because they appeared to have a large amount of particulate matter on them (photographs were not available to include in this report). For this reason it was

decided to weigh the filters in an attempt to estimate exposure to total particulate matter. Since the filters were not pre-weighed, six new filters were weighed from the same pack to establish a tare weight. The weight of the filter from position 1 was significantly different from the mean so that <5% of the time we would be wrong in making that assumption. The difference between the mean filter weight and that of position 1 was 24.540 mg. This calculates to an exposure level of 12,649 mg/m^3. This is considerably higher than the OSHA PEL TWA of 15 mg/m^3 (see attachment J-1). The weight of the filter from position 2 was not significantly different from the mean.

The data from the two thermocouples was recorded at 10-sec. intervals. The figure below shows that the 3-ft. extension successfully cooled the sample gases prior to entering any of the sampling devices.



After the first test one of the 9-ft. line was rinsed with 10 mL of 0.1 M KOH. After test 2 both of the 9-ft. stainless steel sample lines were rinsed. For the second test both of the rinses has a yellow tinge; however, line 2 rinse was much darker. Analysis of all three samples for anions by ion chromatography showed a small amount of chloride and a very large amount of sulfate ion. The amount of HCN measured in the rinse samples represented only a few percent of the total HCN measured.

Two foam samples, one unburned and one partially burned, from the test on 5 Sept 03, were submitted to the FTIR lab at the Aberdeen Test Center for analysis. The pyrolysis and combustion analysis both showed the presence of hydrogen cyanide and organo ioscyanates, which could include methyl isocyanate. According to NIOSH and OSHA methyl isocyanate is much more of an exposure hazard than hydrogen cyanide (Appendix FF-2 and FF-3).

The attached report summarizes the FTIR work. This FTIR technique could be a valuable tool for predicting the types of compounds to sample for prior to conducting the actual test burn. In this way the proper sampling devices could be obtained and the calibration ranges could be adjusted to match anticipated levels of combustion products produced in a fire.

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J.2 NIOSH POCKET GUIDE TO CHEMICAL HAZARDS

J.2.1 Particulates not otherwise regulated

CAS RTECS

Synonyms & Trade Names
"Inert" dusts, Nuisance dusts, PNOR [Note: Includes all inert or nuisance dusts, whether mineral, inorganic, not listed specifically in 1910.1000.]

DOD ID & Guide

Exposure Limits
NIOSH REL: See Appendix D

OSHA PEL: TWA 15 mg/m^3 (total) TWA 5 mg/m^3 (resp)

IDLH N.D. See: IDLH INDEX

Conversion

Physical Description
Dusts from solid substances without specific occupational exposure standards.

Properties vary depending upon the specific solid.

Incompatibilities & Reactivities
Varies

Measurement Methods
NIOSH 0500, 0600
See: NMAM or OSHA Methods

Personal Protection & Sanitation
Skin: No recommendation
Eyes: No recommendation
Wash skin: No recommendation
Remove: No recommendation
Change: No recommendation

First Aid (See procedures)
Eye: Irrigate immediately

Breathing: Fresh air

Important additional information about respirator selection
Respirator Recommendations To be added later

Exposure Routes inhalation, skin and/or eye contact

Symptoms Irritation eyes, skin, throat, upper respiratory system

Target Organs Eyes, skin, respiratory system

See also: INTRODUCTION

J.2.2 Methyl isocyanate

CAS 624-83-9

CH_3NCO RTECS NQ9450000

Synonyms & Trade Names

Methyl ester of isocyanic acid, MIC **DOT ID & Guide** 2480 155

Exposure Limits NIOSH REL: TWA 0.02 ppm (0.05 mg/m^3) [skin]

OSHA PEL: TWA 0.02 ppm (0.05 mg/m^3) [skin]

IDLH 3 ppm See: 624839 **Conversion** 1 ppm = 2.34 mg/m^3

Physical Description: Colorless liquid with a sharp, pungent odor.

MW: 57.1 BP: 102 - 104°F FRZ: -49°F Sol (59°F): 10% VP: 348 mmHg IP: 10.67 eV

Sp.Gr: 0.96 Fl.P: 19°F UEL: 26% LEL: 5.3%

Class IB Flammable Liquid: Fl.P. below 73°F and BP at or above 100°F.

Incompatibilities & Reactivities
Water, oxidizers, acids, alkalis, amines, iron, tin, copper [Note: Usually contains inhibitors to prevent polymerization.]

Measurement Methods
OSHA 54
See: NMAM or OSHA Methods

Personal Protection & Sanitation
Skin: Prevent skin contact
Eyes: Prevent eye contact
Wash skin: When contaminated
Remove: When wet (flammable)
Change: No recommendation
Provide: Eyewash, Quick drench **First Aid** (See procedures)
Eye: Irrigate immediately
Skin: Water flush immediately
Breathing: Respiratory support
Swallow: Medical attention immediately

Important additional information about respirator selection
Respirator Recommendations NIOSH/OSHA
Up to 0.2 ppm: (APF = 10) Any supplied-air respirator*
Up to 0.5 ppm: (APF = 25) Any supplied-air respirator operated in a continuous-flow mode*
Up to 1 ppm: (APF = 50) Any self-contained breathing apparatus with a full facepiece/(APF = 50) Any supplied-air respirator with a full facepiece
Up to 3 ppm: (APF = 2000) Any supplied-air respirator that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode
Emergency or planned entry into unknown concentrations or IDLH conditions: (APF = 10,000) Any self-contained breathing apparatus that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode/(APF = 10,000) Any supplied-air respirator that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained positive-pressure breathing apparatus
Escape: (APF = 50) Any air-purifying, full-facepiece respirator (gas mask) with a chin-style, front- or back-mounted organic vapor canister/Any appropriate escape-type, self-contained breathing apparatus

Exposure Routes inhalation, skin absorption, ingestion, skin and/or eye contact

Symptoms Irritation eyes, skin, nose, throat; respiratory sensitization, cough, pulmonary secretions, chest pain, dyspnea (breathing difficulty); asthma; eye, skin damage; in animals: pulmonary edema

Target Organs Eyes, skin, respiratory system See also: INTRODUCTION See ICSC CARD: 0004 See MEDICAL TESTS: 0143

J.2.3 Hydrogen cyanide

CAS 74-90-8

HCN **RTECS** MW6825000

Synonyms & Trade Names

Formonitrile, Hydrocyanic acid, Prussic acid

DOT ID & Guide

1051 117 (>20% solution)
1051 117 (anhydrous)
1613 154 (</=20% solution)

Exposure Limits

NIOSH REL: ST 4.7 ppm (5 mg/m^3) [skin]

OSHA PEL†: TWA 10 ppm (11 mg/m^3) [skin]

IDLH 50 ppm See: 74908 **Conversion** 1 ppm = 1.10 mg/m^3

Physical Description
Colorless or pale-blue liquid or gas (above 78°F) with a bitter, almond-like odor. [Note: Often used as a 96% solution in water.]

MW: 27.0 BP: 78°F (96%) FRZ: 7°F (96%) Sol: Miscible VP: 630 mmHg IP: 13.60 eV

Sp.Gr: 0.69 Fl.P: 0°F (96%) UEL: 40.0% LEL: 5.6% Class IA Flammable Liquid Flammable Gas

Incompatibilities & Reactivities
Amines, oxidizers, acids, sodium hydroxide, calcium hydroxide, sodium carbonate, caustics, ammonia [Note: Can polymerize at 122-140°F.]

Measurement Methods
NIOSH 6010
See: NMAM or OSHA Methods

Personal Protection & Sanitation
Skin: Prevent skin contact
Eyes: Prevent eye contact
Wash skin: When contaminated
Remove: When wet (flammable)
Change: No recommendation
Provide: Eyewash, Quick drench **First Aid** (See procedures)
Eye: Irrigate immediately
Skin: Water flush immediately
Breathing: Respiratory support
Swallow: Medical attention immediately

Important additional information about respirator selection
Respirator Recommendations NIOSH
Up to 47 ppm: (APF = 10) Any supplied-air respirator
Up to 50 ppm: (APF = 25) Any supplied-air respirator operated in a continuous-flow mode/(APF = 50) Any self-contained breathing apparatus with a full facepiece/(APF = 50) Any supplied-air respirator with a full facepiece
Emergency or planned entry into unknown concentrations or IDLH conditions: (APF = 10,000) Any self-contained breathing apparatus that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode/(APF = 10,000) Any supplied-air respirator that has a full facepiece and is operated in a pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained positive-pressure breathing apparatus
Escape: (APF = 50) Any air-purifying, full-facepiece respirator (gas mask) with a chin-style, front- or back-mounted canister providing protection against the compound of concern/Any appropriate escape-type, self-contained breathing apparatus

Exposure Routes inhalation, skin absorption, ingestion, skin and/or eye contact

Symptoms Asphyxia; lassitude (weakness, exhaustion), headache, confusion; nausea, vomiting; increased rate and depth of respiration or respiration slow and gasping; thyroid, blood changes

Target Organs central nervous system, cardiovascular system, thyroid, blood

See also: INTRODUCTION See ICSC CARD: 0492 See MEDICAL TESTS: 0117